PATENT SPECIFICATION (11) 1281381

NO DRAWINGS

(21) Application No. 12589/69 (22) Filed 10 March 1969
(31) Convention Application No. 713231 (32) Filed 14 March 1968
(31) Convention Application No. 763931 (32) Filed 30 Sept. 1968
(31) Convention Application No. 763967 (32) Filed 30 Sept. 1968 in
(33) United States of America (US)
(45) Complete Specification published 12 July 1972
(51) International Classification C08G 53/20 37/00 51/00//C08F 47/00
(52) Index at acceptance

C3R 1C16 1C5B2 1C6X 1C8P 1E2B 1EX 1L2B 1L2CX 1L4C 29C6X 29C8P 29L2CX 29L4C 29T2 2C6X 2C8P 2L2CX 2L4C 2T2
B2E 378 419 41X 41Y 44Y 457 458 462 463 464 46Y 473 474 485 486 487 498 570
C1A D46 G16 G16D46 G46 G46D46 G47 G47D46 G48 G48D46 G51 G51D46
C1H DX
C3C 1C R1F
C3P 4C8B 4D2 4D3A 4D3B1 4T1X

1281381

(54) METHOD FOR PRODUCING A HEAT BARRIER

(71) I, RUDY W. GUNNERMAN, a citizen of the United States of America, of 535 Haynes Avenue, Beverly Hills, State of California, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to alkali earth sulfides and method of making the same

A heat barrier is formed which upon the application of heat thereto results in the surface formation upon that composition of an alkali earth sulfide produced as a result of the application of a high temperature atmosphere on such surface causing a reaction to take place between alkali earth sulfates and the constituents of thermosetting plastics which have been intermittently mixed with the alkali earth sulfates with the result that a surface reaction occurs producing an adherent heat retardant condition upon the surface of the composition and which resists the transmission of heat into the composition and further is resistant to the erosion of the surface

Alkali earth sulfides have relatively high indices of refraction The alkali sulfides are here produced by reacting alkali earth sulfate hydrates in which are intermittently mixed thermosetting plastics which are reacted at high temperatures to reduce the hydrated sulfates to the alkali earth sulfides as a surface condition upon the admixture of the alkali earth sulfides and thermosetting plastics as an adherent heat rejecting barrier

This invention relates to the production and use of a heat barrier composition which is effective to prevent the transmission of heat and results in the production of a condition upon the surface of the composition which acts as a heat barrier over relatively long periods of time and at the same time produces upon the surface of the composition a material or condition which resists erosion of the surface.

I have discovered that an effective heat barrier can be produced upon the surface of a composition consisting of alkali earth sulfates and thermosetting plastics which are intimately admixed and where upon the application of heat to such composition the thermosetting plastics disintegrate in such manner as to result, upon the continued application of heat thereto, in a reducing action within the composition whereby the sulfates are reduced to the sulfides as primarily a surface reaction.

I have further discovered that upon the formation of such surface sulfides upon the surface of the composition that heat penetration into the composition is so reduced as to effectively retard or prevent disintegration of the thermosetting plastics and thereby prevent further reduction of the sulfates to the sulfides so that erosion of the material upon such application of heat is effectively controlled.

I have also discovered that the alkali earth sulfides formed upon the surface of such composition under the extreme heat application thereto provided by the arc plasma jet flames which result in the formation of the sulfide glaze or film upon the surface produces a surface condition where further heat penetration into the composition is inhibited to such a degree that the back surface of even

a thin layer of that composition does not rise materially in temperature even on prolonged application of such heat condition to the surface thereof.

I have also discovered that the same formation of the alkali sulfide upon the surface of such composition where acetylene gas torch flames are applied directly to such surface results in the same apparent rejection of the heat flow into the material. I have also found that the same results are accomplished through application of any other high temperature atmosphere applied to the surface such, for example, as are existent in the exhaust at the firing of rocket engines or the like

There has long been sought a preparation or composition which would be effective as a heat barrier to prevent transmission of heat from one surface to another and which, for example, might be effectively used under conditions where high velocity, high temperature gas flames or the like are applied to a surface and which would be effective to prevent the heat so transmitted to said surface from being transmitted through the said material. I have discovered that I am able to produce such a material by the formation in position of alkali earth sulfide glazes upon such surface and which apparently act through the property of reflection or dispersion of the heat so that the same is reflected or dispersed away from the surface so formed rather than being transmitted therethrough.

I have further found that the formation of the sulfide upon the surface of such composition is a surface condition in that the material is not seriously eroded during such application of high temperature to its surface due, I believe, to the fact that when the sulfides are formed upon the surface they act to either reflect or disperse the heat so that the heat flow into the composition is at such a rate that the temperature of the material underlying such sulfide surface does not rise to the point that further sulfides are formed thereunder

In carrying out my invention I intimately mix alkali earth sulfates with fine particles of thermosetting plastic wherein the alkali earth sulfates upon taking on water of crystallization form a matrix to hold the fine particles of thermosetting plastic in intimate contact with the alkali earth sulfates so that application of high temperature, high velocity reducing atmospheres to the surface at or near their temperature of heat destruction provides the reducing agents, principally carbon, necessary to react with the sulfates to reduce the sulfates to the sulfide forming what is apparently a glaze of said sulfides which is, I have found, extremely efficient in reflecting or dispersing heat so that it does not penetrate the composition prepared

Calcium sulfate, i.e. gypsum ($CaSO_4, 2H_2O$) is mixed with water to form a slurry using the same proportions of gypsum and water as is ordinarily used in forming a slurry for casting purposes. The slurry thus formed is allowed to stand for such period of time as will permit the addition thereto of phenolic resin either in finely ground condition or as microballoons without the tendency of the said phenolic resin to separate during the subsequent setting, i.e., crystallization of the gypsum, which thereby forms a matrix holding the phenolic resin intimately dispersed with the calcium sulfate throughout the composition. In this composition I employ in this specific example 30% by volume of gypsum and 70% by volume of finely divided phenolic resin and the amount of water added to form the slurry is in accordance with good practice that amount which will permit the formation of a thick cream slurry, i.e., in most cases employing the minimum of water which will permit the formation of a uniform intimate mixture of the gypsum and phenolic resin. The ratio of gypsum, phenolic resin and water employed in forming the composition may, of course, be varied depending on the density of the mixture desired for the conditions of application or use desired and is not herein set forth as a limitation of the proportions of ingredients used in carrying out my invention.

I have similarly prepared compositions employing beryllium sulfate, magnesium sulfate, strontium sulfate, and barium sulfate, and phenolic resin, and others of the thermosetting plastics.

In producing the composition embodying my invention so that it will have flexibility as distinguished from rigid compositions produced by the above set forth example, I have in a similar manner produced the slurry of the alkali earth sulfate and water and thermosetting plastic and have added thereto a suspension of polyvinyl acetate and have found that the composition thereby produced is flexible as distinguished from a rigid composition, the specific example of which is, I have mixed 100 parts by volume of gypsum, sufficient water to form the slurry as above described, to which I have added 200 parts by volume of phenolic resin, and 100 parts by volume of the approximately 50% suspension of polyvinyl acetate in water and have found that upon setting of the alkali earth sulfate, that is, upon its crystallization to form the matrix holding the plastics in intimate association with the calcium sulfate of composition, the resultant composition was flexible as distinguished from the rigid composition produced by the first stated example. The operation apparently performed in this example is that the addition of the vinyl plastics to the composition in excess of that set forth in the first example given has prevented the complete interlock of the crystals of the alkali earth sulfate, leaving the composition flexible.

I have further found that the degree of sub-

division of the thermosetting plastics employed in forming the composition of my invention is of importance only in that if relatively large particles of the thermosetting plastic are present, upon the application of the high temperature reducing flame to the surface of such composition a tendency has been found to exist to ignite such large particles but except for such unwanted burning upon the surface there has been no observable effect upon the formation of the alkali sulfide glaze upon the surface of the composition or the rate of erosion thereof. The specific tests which have been carried out of the composition embodying my invention are exemplified by the following:

A test block of the composition was prepared in the manner hereinabove set forth in which proportions were 70% by volume of phenolic resin microballoons to 30% by volume of gypsum with water which was allowed to set to form test blocks which were 2"×2" square of 1/2" thickness. The arc plasma jet flame was applied to the surface of such block under the following conditions:

Heat flux (Btu/ft^2-second)	1000
Gas Enthalpy (Btu/lb)	6050
Test Duration in seconds	24
Stagnation Pressure (psig)	1.242
Gas Temperature (°F.)	10025
Gas Velocity (ft/second)	1913

with the following results:

Decrease in weight (grams)	4.787
Percentage decrease in weight	3.4
Depth of erosion in inches in the surface so exposed	0.199

Final temperature in °F.

(a) Back Face	140°
(b) Front Face (Optical)	4820
(c) Front Face (Total Radiation)	4340

Further tests were conducted in blocks of the same composition to determine the rate of erosion of the surface with the following results:

Specimen	Heat Flux (Btu/ft^2 sec)	Test Time (sec)	Erosion Rate (mil/sec)
A	100	137	3.27
B	500	24	3.96
C	500	44	7.70
D	1000	24	8.30

Further tests were conducted employing larger sheets of the same composition of like thickness which were tested in an oven over propane gas burners which were spaced 18" on center and where the burners were placed 30" from the face of the test panel. Propane gas was burned in the burners under the conditions hereinafter set forth. The temperatures at the face of the panel, the face toward which the flames were directed were measured by means of 8 Chromel-Alumel thermocouples encased in 1/2 inch iron pipe and placed approximately 6" from the panel face. (The words "Chromel" and "Alumel" are registered Trade Marks). The vertical and lateral placement of the thermocouples was determined by experimentation and visual observation of the flow pattern. Thermocouple leads were connected to a rotary switch and readings were taken manually from a Technique Associates Pyrotemp Model o-B pyrometer. The backside temperatures were taken by placing seven iron-constatan thermocouples on the cross framing of the panel and with one couple placed directly on the back surface of the composition. The following temperature readings in degrees Fahrenheit were taken from the panel face:

Temperature Readings, Degrees F.
Panel Face

Minutes	Station No. 1	2	3	4	5	6	7	8	Required Temp.
2	250	200	164	164	204	174	115	158	—
5	490	—	—	—	—	—	—	—	1000
7	760	605	334	273	630	555	300	280	1150
12	1020	870	590	—	—	—	—	—	1340

The pressure of the gas flowing to the burners at the start of the test was five pounds per square inch which was increased to ten pounds per square inch after five minutes at which gas pressure the test was continued for the full duration of twelve minutes.

The temperature at the back of the panel taken through the distribution of the thermo-

couples as above described were as shown by the following table:

Temperature Readings, Degrees F.

	Panel Back	
Minutes	Min.	Max.
0	87	102
2	87	102
4	90	103
6	90	110
8	87	109
10	92	112
12	92	113
14	93	124
16	94	126
18	76	108

Further tests utilizing substantially the same equipment and test samples of the same character have been conducted wherein for a total elapsed time of two hours and fifteen minutes the average surface temperatures taken over the surface have been in excess of 1900°F. and the temperature of the back face taken likewise over the distributed points as hereinabove indicated has been less than 180°F.

In order to account for the unexpected results, i.e., the formation of the thin adherent heat rejective sulfide on the surface, and the fact that this material under these conditions exhibits these unusual properties of heat rejection, I have endeavored to determine as nearly as possible the phenomena occurring under the conditions as set forth. It appears fundamentally that the reaction which is occurring under the reducing influence of the heat application to the surface is that the calcium sulfate is reduced to calcium sulfite principally through the action of chemically active carbon in intimate contact with the sulfate. When this contact is maintained under the heat conditions defined there is a direct reduction to the sulfide principally through the formation of carbon dioxide liberated from the surface after or perhaps simultaneously with the formation and liberation from the material of water in the form of steam and the formation of some carbon monoxide and traces of what I am unable to explain of methane (CH_4) which is found by analysis of the gas leaving the surface of the material under the conditions hereinabove defined, indicating that there is present under the conditions of these tests an excess of reducing capacity. The primary reaction may be, in a somewhat simplified form, indicated by the following:

$$\underset{\text{(Phenolic Resin)}}{1C_{21}H_{24}O_4} + \underset{\text{(Gypsum)}}{10CaSO_4 . 2H_2O} \xrightarrow[\text{(1000°F.—2300°F.)}]{\text{Flame}}$$

$$\longrightarrow \underset{\text{(Calcium Sulfide)}}{10Cas} + 32H_2O + 16CO_2 + 5C + \underset{\text{(trace)}}{CO} + \underset{\text{(trace)}}{\text{Hydrocarbon}}$$

In the above equation, I have not endeavored to fully balance the equation because of the fact that gas analysis of the gas formed upon that surface will show variable quantities of the respective gases produced dependent upon the time when the gas samples were taken from the surface. Fundamentally these same reactions occur in employing the hydrates of beryllium sulfate or magnesium sulfate with or without strontium sulfate and/or barium sulfate added thereto and with phenolic resin or other thermosetting plastics, and would logically follow with reference to radium sulfate although due to the expense and my inability to obtain samples and the highly dangerous nature of this intensely radioactive material, I have not actually been able to establish that radium sulfate would in all respects act in the same manner as the other members of the No. 2-A grouping of the Periodic Table.

It further appears that the active ingredient of the phenolic resin in carrying out this extremely difficult reducing action is brought about by that portion of the phenolic resin represented by CHOH or the equivalent radical of the other thermosetting resins. It is possible in this reaction that that portion of the phenolic resin represented by the C_6H_5OH, i.e., the phenol, may leave the reacting area and the breakdown of the phenolic resin under the heat conditions with or without materially affecting the reaction, i.e., the reduction of the calcium sulfate to sulfide.

Further tests were conducted by the direct application of water to the surface of the block immediately after discontinuing the application of the high velocity, high intensity reducing flame to the surface with the intersecting result that practically no steam is emitted from the surface, apparently establishing the fact that the composition of my invention has not retained a high quantum of heat.

It has been found that upon the cooling of the composition after the formation of the calcium sulfide barrier upon its surface where the cooling has been permitted to take place in the atmosphere that there is a deterioration

of the adherent calcium sulfide glaze upon the surface apparently due to its reaction with the water of the air resulting in the formation upon the surface of calcium oxide and free sulfur and perhaps calcium hydroxide along with some residual calcium sulfide depending upon the period of time when the observation is made. The material thus remaining upon the surface after exposure to the hydration by the water in the air is a white powdery material together with the free sulfur as indicated and this material is no longer tightly adherent to the surface. The disintegration of the surface condition which takes place when exposed to the water of the atmosphere has been found, however, to have no appreciable effect upon the composition embodying my invention in that when the surface of such composition is subjected to like heat conditions as hereinabove set forth the thin adherent coating of alkali earth sulfide will again form upon the surface of the composition forming the same heat barrier characteristics hereinabove defined.

Where phenolic resin is employed in the preparation of the composition embodying my invention it may be in the form of a powder or granules of phenolic resin produced by grinding or reducing the particle size of Bakelite (the word "Bakelite" is a registered Trade Mark) or may be in the form of phenolic microballoons produced in accordance with the disclosure of Patent No. 2,797,210 above referred to. As reported in said patent, the microballoons have a very minute particle size with relatively low bulk density. The fact is, however, that the phenolic resin has been expanded by "ballooning" and has not been found to have any material effect upon the properties hereinabove referred to.

Further, the novelty of my invention lies in the use of thermosetting plastics in such composition wherein at the temperature of disintegration of such composition the carbon resulting from such disintegration acts as the primary reducing agent and in that this rate of disintegration of the thermosetting plastic is retarded by the heat barrier characteristics by the formation of the thin layer of sulfide upon the surface of the composition.

In carrying out the method embodying my invention I have found that I may employ any thermosetting plastic which possesses the property of heat destruction as opposed to melting or boiling at elevated temperatures. Among the thermosetting plastics I may employ are the phenolic resins, urea formaldehydes, melamine formaldehydes and diallyl phthalate polymers or prepolymers. The above specific plastics are set forth as examples only and not as limitations of the thermosetting plastics which may be used, the necessary factor of which is that upon application of heat thereto the thermosetting plastics disintegrate to provide carbon in intimate contact with the sulfate to carry out the reduction reaction.

I have found also that like intimate mixtures of alkali earth sulfides and other carbonaceous materials as plastics which are not thermosetting, such for example as polyvinyl acetates, have a tendency to burn and immediately form carbon on the surface of the material to disintegrate the composition and apparently do not result in the formation of a sulfide adherent layer or glaze and therefore do not act to control the rate of the reaction occurring in the composition and/or the rate of erosion thereof. The tendency observed is that in such other carbonaceous material the material apparently melts, boils or disintegrates and burns upon the surface as distinguished from the unexpected property observed herein of the formation of the adherent layer, film, or glaze of sulfide upon the surface where the thermosetting plastics are used and the controlled rate of reaction due to such glaze of sulfide acting to either reflect or disperse the heat waves away from the surface of the composition.

I have further observed that it is apparently characteristic of my invention that the primary reducing action accomplished at the controlled rate as herein stated is due to the release of the carbon within the composition at the temperature of disintegration of the thermosetting plastic and as a result of such disintegration.

I have also found that in carrying out the method embodying my invention, I may apply a reinforcing grid prior to the setting of the mixture to resist the formations of fissures or cracks in the composition during the application of heat thereto.

WHAT I CLAIM IS:—

1. A method for producing a heat barrier composed of an alkaline earth sulfide, an alkaline earth sulfate and a source of available carbon, said method comprising the steps of: bonding fine particles of the source of available carbon and alkaline earth sulfate together in an intimate mixture and reacting some of the source of available carbon and alkaline earth sulfate together to form a surface heat barrier consisting of the alkaline earth sulfide in the form of a surface glaze.

2. The method of claim 1 wherein the chemical reaction is a reduction of an alkaline earth sulfate by reaction with carbon to produce alkaline earth sulfide and carbon dioxide.

3. The method of claim 1 or 2 wherein the alkaline earth sulfate employed is derived from the class consisting of beryllium sulfate hydrate, magnesium sulfate hydrate, calcium sulfate hydrate, strontium sulfate and barium sulfate.

4. The method of claim 1, 2 or 3, wherein the source of available carbon comprises thermosetting plastics derived from the class consisting of phenolic resins, urea formaldehyde and melamine formaldehydes which disin-

tegrate upon the application of heat thereto to provide available carbon.

5. The method of claim 1, 2 or 3, wherein the source of available carbon is a thermosetting plastic selected from the group consisting of dialkyl phthalate polymers or prepolymers.

6. The method of claim 4 or 5 wherein the source of available carbon includes polyvinyl acetates in addition to said thermosetting plastics.

7. The method of any one of claims 1 to 6 including the step of applying a reinforcing grid prior to the setting of the mixture to resist the formation of fissures or cracks in the composition during the application of heat thereto.

8. An article formed by the method of any one of claim 1 to 7, comprising an intimate mixture of an alkaline earth sulfate and fine particles of a source of available carbon having upon the surface thereof an adherent layer of alkaline earth sulfide.

9. The article of claim 8 wherein the alkaline earth sulfate is calcium sulfate.

10. The article of claim 8 wherein the alkaline earth sulfate is beryllium sulfate.

11. The article of claim 8 wherein the alkaline earth sulfate is magnesium sulfate.

12. The article of claim 8 wherein the alkaline earth sulfate is strontium sulfate.

13. The article of claim 8 wherein the alkaline earth sulfate is barium sulfate.

14. The article of any one of claims 8 to 13, wherein the source of available carbon is phenolic resin.

15. The article of any one of claim 8 to 13, wherein the source of available carbon is urea formaldehyde.

16. The article of any one of claims 8 to 13, wherein the source of carbon is a diallyl phthalate polymer or prepolymer.

17. The article of any one of claims 8 to 16 wherein there is added a polyvinyl acetate which acts to reduce the crystal interlock.

18. The method of claim 1, wherein said intimate mixture comprises a substantially uniform mixture of fine particles of phenolic resin balloons incorporated in a matrix of gypsum and water.

19. The method of claim 18 wherein the ratio is 70% by volume of phenolic resin balloons to 30% by volume of gypsum.

20. The method of claim 18 in which the ratio by volume of phenolic resin to gypsum is related to the density of the mixture.

21. A method for producing a heat barrier substantially as herein described.

22. An article having an adherent alkaline earth sulfide surface thereon substantially as herein described.

STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
5, Quality Court,
Chancery Lane,
London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.